

## ISOTHERMAL OXIDATION BEHAVIOUR OF A POLYMER-DERIVED AMORPHOUS Si/C/N CERAMIC

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**ABSTRACT:** Polymer-derived non-oxide ceramics are candidate materials for various applications especially in the high-temperature regime above 1200°C, where conventionally liquid-phase sintered ceramics start to fail due to softening of their glassy grain boundary phase. The polymer-to-ceramic approach uses high-purity educts from polymer chemistry. It allows for an additive-free synthesis of ceramic materials and thus avoids the presence of glassy grain boundary phases in the body. In this work, the oxidation behaviour of poly(hydridomethyl)silazane NCP200-derived ceramic materials is investigated in more detail. Therefore, after standardised crosslinking and ceramisation the amorphous ceramic material was milled and sieved to a powder fraction with  $r \leq 32\mu\text{m}$ . These powders with high surface-to-volume ratio were isothermally oxidised for 20 h using a TGA at temperatures between 1000°C and 1500°C in steps of 100K, each a sample of approx. 120mg in an alumina crucible. Preliminary results on the oxidation behaviour of the specimens are reported and the mechanisms of oxidation are outlined.

**KEY WORDS:** polymer-derived ceramic, silicon carbide nitride ceramic, SiCN, isothermal oxidation

### 1. INTRODUCTION

Non-oxide ceramics are of ongoing interest for applications under thermo-mechanical loads and severe environmental conditions. The high-temperature oxidation resistance of silicon-based non-oxide ceramics depends on the formation of protective oxide scales. Polymer-derived non-oxide ceramics are promising candidate materials for high-temperature applications, as they are free of oxide-based grain boundary phases failing service due to softening at considerably lower temperatures as the non-oxide material itself. Furthermore, silicon carbonitrides (SiCN) are a class of materials that show extremely high glass transition temperatures in the range of 1500°C, slow rates of crystallisation and extraordinary high creep resistance [1].

Asides the thermal load, usually environments with aggressive gases and possible corrosive deposits are encountered. The most obvious corrosive constituent of hot gasses in combustion environments like from energy conversion machines are oxygen, water, and oxides of carbon as well as nitrogen. Most studies focus on oxidation behaviour in pure oxygen and dry or wet air. Early oxidation experiments of polymer-derived SiCN materials investigated the influence of the microstructure on oxidation behaviour [2] and oxidation kinetics [3]. First oxidation experiments employing a solid amorphous ceramic body of low open porosity obtained from the poly(hydridomethyl)silazane NCP200 at 1500°C, revealed the formation of a self-passivating surface layer [4]. A consecutive study on disk-shaped as well as powdered NCP200-derived samples at 1350°C in ambient air reported parabolic oxidation behaviour and phenomenological similarities to the oxidation behaviour of reaction-bonded silicon nitride (RBSN) [5].

In this work we report on the isothermal oxidation behaviour of a NCP200-derived amorphous SiCN ceramic material covering the temperature range from 1000°C to 1500°C in steps of 100 K. Special attention is put to the discussion of prominent effects occurring in the temperature range of 1100°C to 1300°C.

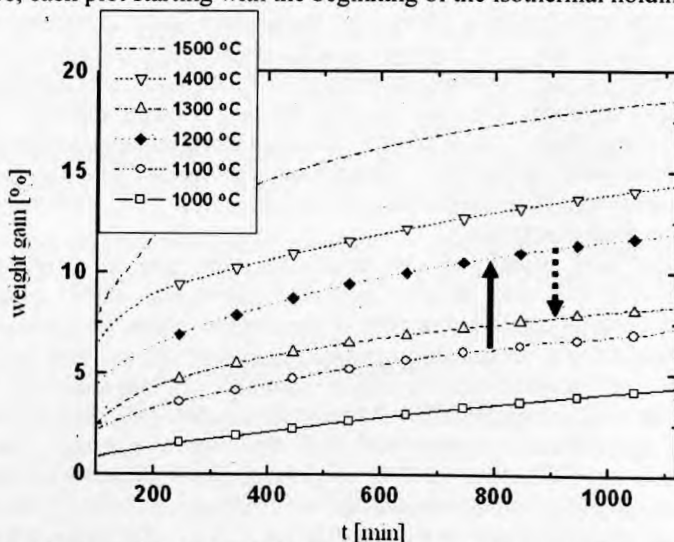
## 2. MATERIAL AND METHOD

The material used in this work has been produced by a standard procedure with cross-linking of the as-delivered NCP200 polymer at 400°C for 3 h in flowing Ar and 1 h under vacuum, followed by pyrolysis at 1100°C for 4 h under flowing Ar. For a more detailed description of the processing and polymer-to-ceramic conversion see reference [6]. The resulting amorphous SiCN material has been analysed by hot gas extraction method to reveal its stoichiometry to be  $\text{Si}_{2.02}\text{N}_{1.95}\text{C}_{1.12}\text{O}_{0.09}\text{H}_{0.29}$ . After milling and sieving to a powder fraction  $< 32\ \mu\text{m}$  with  $d_{50} = 16.5\ \mu\text{m}$  under inert atmosphere (dry nitrogen) a BET analysis was conducted to determine the surface area of the powder to be  $1.08\ \text{m}^2/\text{g} \pm 0.02\ \text{m}^2/\text{g}$ . The pyknometric density of the powder was  $2.23\ \text{g}/\text{cm}^3 \pm 0.005\ \text{g}/\text{cm}^3$ .

Some 122 mg of the powder were each weighed into a standard STA (simultaneous thermal analysis) alumina crucible. The isothermal oxidation was conducted in a Netzsch STA 429 with open gas outlet to freely exchange ambient air of  $42\% \pm 2\%$  relative humidity at 25°C. The heating rate up to the respective isothermal dwelling temperature was 20 K/min. The weight change was recorded continuously by the thermogravimetry module of the STA. From the stoichiometry a total weight gain of 23.2 wt% for complete oxidation of the material was calculated.

## 3. RESULTS AND DISCUSSION

All samples have in common a weight loss of approx. 0.9 wt% in the temperature range of approx. 320°C to approx. 580°C. This is predominantly caused by burning wear debris from the high density polyethylene milling vessels and contingently free carbon on the sample surfaces in oxygen. Around 700°C weight gain sets on, which exhibits the same characteristics for all samples and marks the onset of the oxidation process. Figure 1 shows the respective thermogravimetry plots for each holding temperature, each plot starting with the beginning of the isothermal holding time.

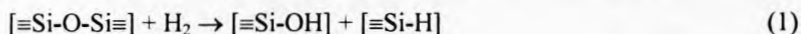


**Fig. 1:** Weight gain of the samples during isothermal holding at the respective oxidation temperatures. Note the significant increase in weight gain from 1100°C to 1200°C and the inversion of order from 1200°C to 1300°C.

None of the samples shows a linear dependency of weight gain on isothermal holding. Two distinct features of Fig. 1 are the significant increase of the weight from 1100°C to 1200°C and the inversion of order from the 1200°C samples to the 1300°C samples, i.e. a lower weight gain for the samples held at the higher temperature.

### 3.1 Temperature below or equal to 1200°C

As shown in [7], NCP200-derived materials contain approx. 5.2 at% hydrogen after pyrolysis under Ar at 1000°C and approx. 0.9 at% hydrogen after annealing under N<sub>2</sub> for 50 h at 1300°C. With various other polycarbosilazane-derived materials annealed under N<sub>2</sub> for 1 h at 1300°C a hydrogen content of 5.5 at% was found [8]. In the respective temperature regime the evolution of H<sub>2</sub> and H<sub>2</sub>O from the samples causes a significant decrease of the viscosity of the forming amorphous surface SiO<sub>2</sub>-layer by the formation of so-called wet glass. This effect already was reported in 1935 [9] and reconfirmed later on in [10]. By this the diffusion of oxygen into the reaction zone, usually seen as the rate limiting step, is massively facilitated and the reaction rate increased. More recent investigations comprehensively substantiate that H<sub>2</sub>O in glasses lowers their melting point [11] and viscosity [12] but also increases their tendency of devitrification [13]. It has been shown that hydrogen dissolves physically as molecule at interstices of the SiO<sub>2</sub>-continuous random network (CRN) as well as chemically through dissociation under formation of hydroxyl groups and hydrides [14, 15]:



Molecules of water also react with SiO<sub>2</sub> under cleavage of Si-O-Si-bridges to form terminating hydroxyl groups:



With increasing temperature the chemical reaction leads to a weakened CRN of low viscosity. The overall effect is a significantly increased oxidation rate at 1200°C.

### 3.2 Temperature equal to or above 1300°C

According to [16], at 1205°C the glass transition temperature  $T_g$  of pure SiO<sub>2</sub> is reached. Above this temperature, structural reorganisations of CRNs take place on a reasonable time scale. This in turn is a prerequisite for rapid crystallisation of the respective amorphous phase. Here, according to our preliminary results from powder X-ray diffraction, the crystalline phase formed is  $\beta$ -cristobalite. This has also been expected by considering the close similarity of the short range order of both phases [17]. The rapid crystallisation of the SiO<sub>2</sub>-layer thus is a consequence of a structural relaxation process facilitated by hydrogen and water evolved from the SiCN-materials. Through crystallisation, the rate limiting process of inward diffusion of oxygen is retarded significantly. This is also reflected in the respective activation energies for oxygen diffusion through a SiO<sub>2</sub>-glass at  $T \leq 1350^\circ\text{C}$ ,  $E_A = 113 \text{ kJ/mol}$  [18] and above 1350°C,  $E_A = 298 \text{ kJ/mol}$  [19].

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